Influence of the impurities of platinum on the surface treatment with the repetitive square wave potential sweeping in sulfuric acid

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Pt is considered as the most important catalyst material for polymer electrolyte fuel cells (PEFC). The high cost of platinum limits the commercialization of PEFC. One possible solution of this problem is to maximize the utilization and stability of platinum. Therefore, it is important to investigate the property of surface structure of platinum.

The electrochemical facetting of noble metals (platinum, palladium, rhodium, gold) applying either square wave or triangular periodic potential routines to metal samples immersed in aqueous acids has been extensively investigated since a long time ago [1]. The type and extent of facetting depended on the upper and lower limits of the potential routine, the frequency, the aqueous electrolyte composition, and the duration of the treatment. These experimental conditions have been extensively discussed in a previous publication [2].

Claviller et. al. indicated the preparation of single crystal platinum from the polycrystalline [3]. They indicated that the surface pretreatment in the prepapring single strucure of platinum is infuluence on the electrochemical properties, such as the dsorption-desorption process of hydrogen, adsorption-desorption of the monolayer of the oxgen, and so on. Therefore, we investigated the infuluence of the pretreatment of platinum on s the repetitive square wave potential sweeping (RSWPS).

The specimen is used 99.7 % in purity comercially available platinum wire (0.3 mm in diameter). We adapted the four type of the pretreatment to platinum before RSWPS. These pretreatments are as follows : (1)washed with aceton and then with ion exchanged water (electrode (A)), (2)melted in the natural gas-oxygen flame and annealed in the air atmosphere (electrode (B)), (3)etched with the mixed acid (H_2SO_4:HNO_3=1:1) at 353 K for 30 min (electrode (C)), and (4)melted, annealed, and then etched in the same way (electrode (D)).

RSWPS carried out in the deaerated 0.5 M H_2SO_4 solution as follows:(1)in the case of the change in the crystal orientation, at high potential scan rate (5 kHz) between 0.05 and 1.5 V vs. RHE for 30 min, (2)in the case of the increase of active surface area, at low potential scan rate (10 Hz) between 0.05 and 1.5 V vs. RHE for 24 hours.

The cylic voltamgram of platinum electrode (D) before and after RSWPS for the increse of surface area are shown in Figure 1. The voltamgram charts are indicated that the real surface area of platinum is increased after RSWPS. As for another types of electrode, these results are shown in Table 1. An increase of the real surface area of platinum after RSWPS is not observed on electrode (A), electrode (B). As for electrode (C), the increase is a liitle. Similarly, although the crystal orientation of platinum electrode (D) could be changed by RSWPS as shown in Figure 2, these changes were not obserbed on the electrode (A) and (B). These results are indicated that RSWPS is influenced by the pretreatment of platinum. The impuritites in platinum colud be removed from the surface, resulting in obtaining high pure platinum. The impurities is an obstacle to rearrangement of platinum atom during RSWPS. Therefore, the pretreatment plays an important role on the reconstruction of the surface of surface.

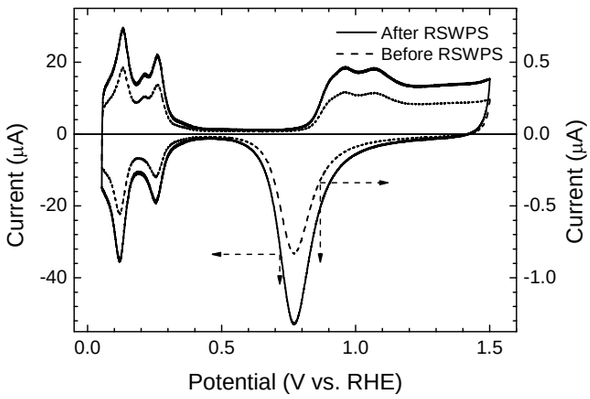

Figure 1. Cyclic voltamgrams of Pt electrodes (D) in 0.5 M H_2SO_4 before and after RSWPS. RSWPS is conducted between 0.05 and 1.50 V at 10 Hz for 24 hours.

Table 1 Real surface area before and after RTPS treatment and relative surface area for platinum.

Electrode	Real Surface Area (cm^2)		Relative Surface Area (−)
	Before RSWPS	After RSWPS	
A	0.536	0.536	1.0
B	0.0798	0.0799	1.0
C	0.145	1.36	9.4
D	0.0630	4.01	63.6

The real surface area of the electrodes was evaluated by integrating the hydrogen adsorption-desorption current-potential curves, assuming that 210 μC/cm^2 for polycrystalline Pt.

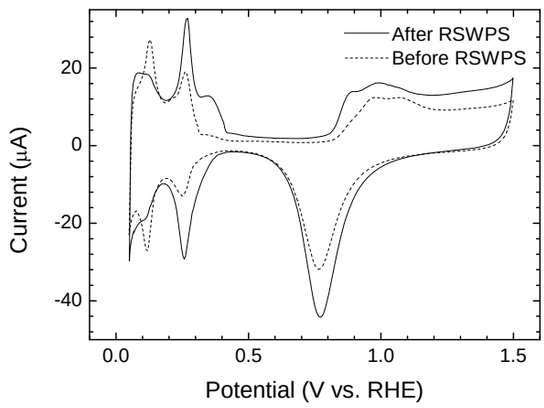

Figure 2. Cyclic voltamgrams of Pt electrodes (D) in 0.5 M H_2SO_4 after RSWPS. RSWPS is conducted between 0.05 and 1.50 V at 5 kHz for 30 min.

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